Title: DEEP DESULFURIZATION OF DIESEL FUEL BY A NOVEL INTEGRATED APPROACH

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ABSTRACT

OBJECTIVE

The overall objective of this project is to explore a new desulfurization system concept, which consists of efficient separation of the refractory sulfur compounds that constitute less than 1 wt% of distillate fuel oil streams by high-capacity selective adsorption, and effective hydrodesulfurization of the concentrated fraction of the refractory sulfur compounds in diesel fuels. In the present period of performance, our approaches focused on 1) identification of the refractory sulfur compounds existing in diesel fuels; 2) preparation of an selective adsorbent and preliminary adsorption experiment; 3) quantum chemical calculation of electron distribution on various alkyl dibenzothiophenes; 4) hydrodesulfurization of the refractory sulfur compounds over CoMo/MCM-41.

ACCOMPLISHEMENTS TO DATE

Identification analysis of the refractory sulfur compounds existing in a current commercial diesel fuel was preformed by using gas chromatograph with a capillary column and a flame photometric detector. The

dominant sulfur compounds found in the diesel fuel are 4-methyl-dibenzothiophene, 4,6-dimethyl-dibenzothiophene, 2,4,6-trimethyldibenzothiophene, 3,6-dimethyldibenzothiophene, 1,4,6-trimethyl-dibenzothiophene, 4-methyl-6-ethyldibenzothiophene, and 1,4/1,6-dimethyldibenzothiophene, in the order of decreasing concentration. A common character in these alkyl dibenzothiophenes is that there are one or two alkyl groups at the 4- and/or 6-positions of dibenzothiophene. Therefore, it is necessary to pay closer attention to these sulfur compounds when the adsorption desulfurization is considered.

An adsorbent (a noble metal compound supported on silica gel) was prepared for adsorption desulfurization. The adsorption experiments using this adsorbent were conducted in a glass column adsorber at ambient temperature and ambient pressure, using both model compounds and real diesel fuel as feeds. The preliminary results show that the concentration of the sulfur compounds in both the model compounds and the diesel fuel decreases significantly after the adsorption treatment, indicating that the sulfur compounds are selectively adsorbed on the adsorbent and the prepared adsorbent works.

Quantum chemical calculations of the electron density on sulfur atom and the electron distribution on molecules of various sulfur compounds were preformed by using a semiempirical method, PM-3 in CAChe MOPAC. The calculation results show that the highest occupied molecular orbital for all alkyl dibenzothiophenes involved in this study is located at the sulfur atom with an π-orbital character. It indicates that the interaction between the sulfur compounds and the adsorbent for selective adsorption would like to occur through such a frontier orbital. According to calculation results, the total electron density on the sulfur atom of various alkyl dibenzothiophenes is almost the same, being around 5.75.

Mesoporous MCM-41 molecular-sieve supported CoMo catalysts with different loading were prepared for hydrodesulfurization of the refractory sulfur compounds. Hydrodesulfurization experiment in a flow reactor system at 350 ßC, 45 atm and 2 h^{-1} LHS was preformed by using 4,6-dimethyldibenzothiophene as a model compound of the refractory sulfur compounds. The hydrodesulfurization results show that at the normal loading of CoMo (13.5 wt% MoO_3, 2.9 wt% CoO), HDS catalytic activity of the CoMo/MCM-41 is similar to that of the CoMo/alumina. However, at the high loading (27.0 wt% MoO_3, 5.8 wt% CoO), the CoMo/MCM-41 displays better HDS catalytic activity for the refractory sulfur compounds than the CoMo/alumina.

FUTUER WORK

We will quantify the concentration of various sulfur compounds in the diesel fuels and the treated diesel fuels. We will improve the currently prepared adsorbent to increase the adsorption capacity, and will develop other potential adsorbents. Another task in our future work is to explore the regeneration methods and regeneration conditions of the adsorbent. We are also interested in examining the effect of the alkyl substituents on the interaction between the sulfur atom in alkyl dibenzothiophene and the active site on the adsorbent surface by a combination of experiment and molecular simulation.

PAPERS PUBLISHED

1. A New Approach to Deep Desulfurization by Adsorption of Sulfur Compounds from Diesel Fuel, Jet Fuel, and Gasoline
   Xiaoliang Ma, Lu Sun and Chunshan Song
   Am. Chem. Soc. Div. Fuel Chem. Prep., 2001, 46 (3-4), to be published. Paper to be presented at an ACS Symposium, Division of Fuel Chemistry, American Chemical Society, National Meeting in Chicago, August 26-31, 2001.

2. Deep Hydrodesulfurization of Diesel and Jet Fuels Using Mesoporous Molecular Sieve-Supported Co-Mo/MCM41 Catalysts.
   Uday Turaga and Chunshan Song
   Am. Chem. Soc. Div. Petrol. Chem. Prep., 2001, 46 (3-4), to be published. Paper to be presented at an ACS Symposium, Division of Petroleum Chemistry, American Chemical Society, National Meeting in Chicago, August 26-31, 2001.

STUDENTS SUPPORTED UNDER THIS GRANT

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